UNIVERSITI SAINS MALAYSIA

Peperiksaan Semester Kedua
Sidang Akademik 2006/2007

April 2007

EKC 107 – Proses Kimia Organik

Masa : 3 jam

Sila pastikan bahawa kertas peperiksaan ini mengandungi SEBELAS muka surat yang bercetak dan SATU muka surat Lampiran sebelum anda memulakan peperiksaan ini.

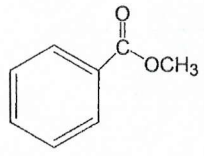
Arahan: Jawab **LIMA BELAS (15)** soalan. Jawab **SEMUA (5)** soalan dari Bahagian A. Jawab mana-mana **LAPAN (8)** soalan dari Bahagian B. Jawab mana-mana **DUA (2)** soalan dari Bahagian C.

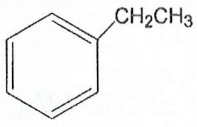
PELAJAR DIBENARKAN MENJAWAB SOALAN SAMA ADA DALAM BAHASA MALAYSIA ATAU BAHASA INGGERIS.

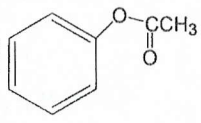
...2/-

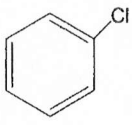
Section A : Answer ALL questions. Each question is worth of 2 marks.
Bahagian A : Jawab SEMUA soalan. Setiap soalan bernilai 2 markah.

1. Which of the following compounds is the most reactive in an electrophilic aromatic substitution reaction with $Cl_2/FeCl_3$?

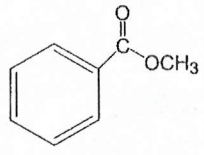
[a] 

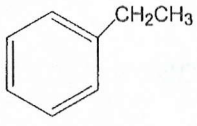
[b] 

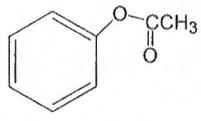
[c] 

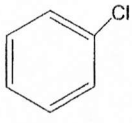
[d] 

1. Sebatian manakah yang paling reaktif dalam tindakbalas penggantian aromatik elektrofilik dengan $Cl_2/FeCl_3$?

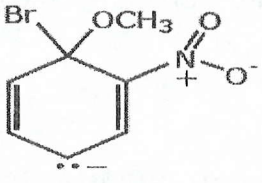
[a] 

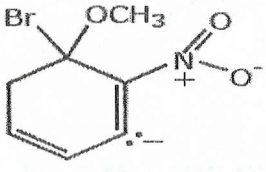
[b] 

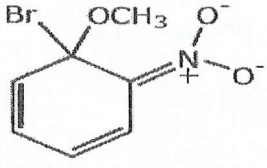
[c] 

[d] 

2. Which of the following is a resonance structure of the intermediate that results when o-nitrobromobenzene is reacted with methoxide anion? (note:lone pairs of electron on oxygens are not shown).

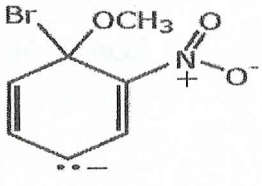
[a] 

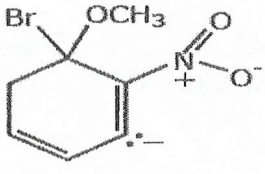
[b] 

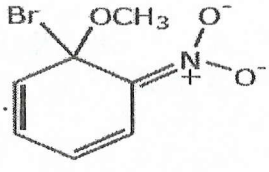
[c] 

[d] [a] and [c]

2. Manakah antara berikut, merupakan struktur resonan perantaraan yang terhasil apabila o-nitrobromobenzena bertindakbalas dengan anion metoksida? (Nota: sepasang elektron tersendiri pada oksigen tidak ditunjukkan).

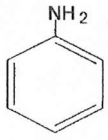
[a] 

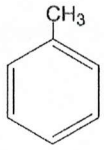
[b] 

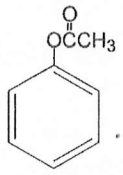
[c] 

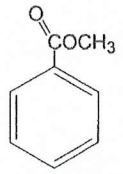
[d] [a] dan [c]

3. Which of the following compounds would be the most reactive in a Friedel-Crafts alkylation reaction?

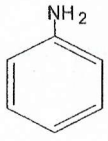
[a] 

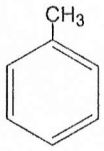
[b] 

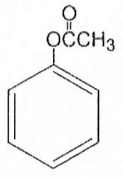
[c] 

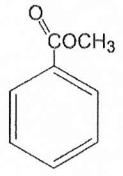
[d] 

3. *Manakah antara sebatian berikut yang paling reaktif dalam tindakbalas pengalkilan Friedel-Crafts?*

[a] 

[b] 

[c] 

[d] 

4. What is the purpose of water added at the end of a Friedel-Crafts alkylation reaction between $CH_3\ CH_2\ CH_2\ Cl/AlCl_3$ and benzene?

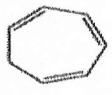
[a] It removes the $AlCl_3$ that complexes with the desired product.
[b] It keeps the alkyl group from rearranging.
[c] It acts as a catalyst to speed up this slow reaction.
[d] It is not actually necessary and therefore not used.

4. *Apakah tujuan penambahan air di akhir tindakbalas pengalkilan Friedel-Crafts di antara $CH_3\ CH_2\ CH_2\ Cl/AlCl_3$ dan benzena?*

[a] Untuk menyingkirkan $AlCl_3$ yang berkompleks dengan hasil yang dikehendaki.
[b] Untuk mengelakkan kumpulan alkil dari penyusunan semula.
[c] Ia bertindak sebagai mangkin bagi mempercepatkan tindakbalas yang perlahan ini.
[d] Ia tidak perlu dan dengan itu tidak digunakan.

5. Which of the following compounds is/are anti-aromatic? Assume that any compound that can become non-planar will do so if "necessary".

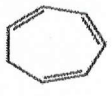
[a] 

[b] 
[c] 

[d] [a] and [c]

5. *Manakah antara sebatian berikut adalah anti-aromatik? Anggapkan bahawa mana-mana sebatian yang boleh menjadi tidak planar akan berbuat demikian jika perlu.*

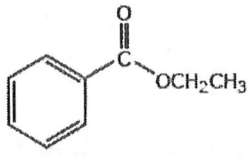
[a] 

[b] 
[c] 

[d] [a] dan [c]

Sections B : Answer any EIGHT questions.
Bahagian B : Jawab mana-mana LAPAN soalan.

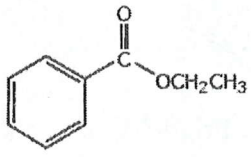
6. Provide the name for the given structure and structure for the name.

[a] 

[b] 3-chloroacetophenone

[5 marks]

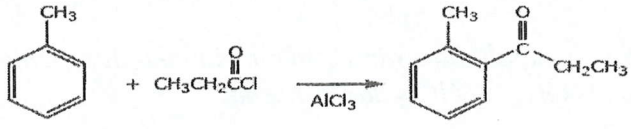
6. *Berikan nama untuk struktur yang diberikan dan struktur untuk nama yang diberikan.*

[a] 

[b] 3-kloroasitofenon

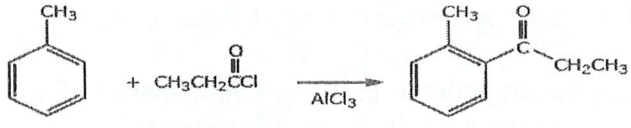
[5 markah]

7. Write a mechanism, including three resonance structures of the organic intermediate formed when the electrophile reacts with the aromatic ring.



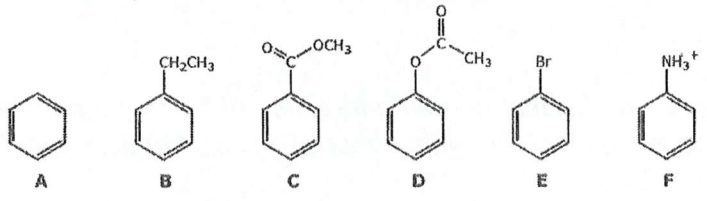
[5 marks]

7. *Tuliskan mekanisma, termasuk tiga struktur resonan bagi pengantaraan organik yang terbentuk apabila elektrofil bertindakbalas dengan gelang aromatik.*



[5 markah]

8. Rank the following compounds from most to least reactive in an electrophilic aromatic substitution with $Br_2/FeBr_3$. You may abbreviate the benzene ring as Ph or use the letters provided for each compound.

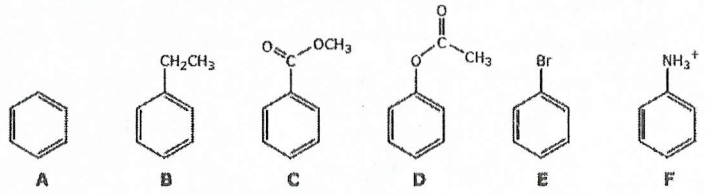


_____ > _____ > _____ > _____ > _____ > _____

most reactive least reactive

[5 marks]

8. *Susun sebatian-sebatian berikut mengikut yang paling reaktif kepada yang kurang reaktif dalam penggantian aromatik elektrofilik dengan $Br_2/FeBr_3$. Anda boleh memendekkan gelang benzena sebagai Ph atau gunakan abjad yang disediakan untuk setiap sebatian.*

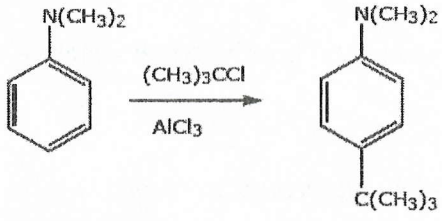


_____ > _____ > _____ > _____ > _____ > _____

paling reaktif kurang reaktif

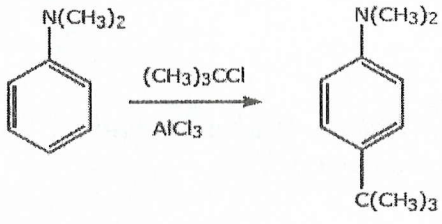
[5 markah]

9. Why the following reaction will not occur?



[5 marks]

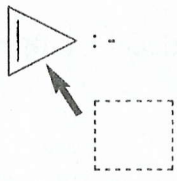
9. *Mengapakah tindakbalas seperti berikut tidak akan berlaku?*

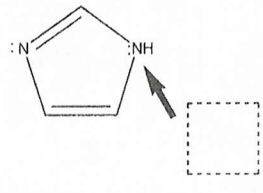


[5 markah]

10. Indicate whether each of the following compounds is aromatic, anti-aromatic, or non-aromatic, and briefly justify your choice. Provide the hybridization of each atom that has an arrow pointing to it and put the hybridization in the box provided. Assume that each carbon atom has enough bonds to hydrogen to complete its octet or to have its formal charge make sense.

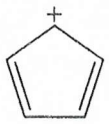
[a] 

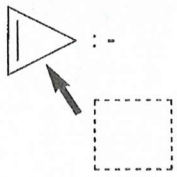
[b] 

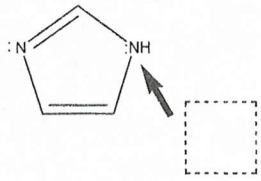
[c] 

[5 marks]

10. *Nyatakan samada setiap sebatian yang berikut adalah aromatik, anti-aromatik atau tak aromatik, dan jelaskan secara ringkas pilihan anda. Berikan penghibridan untuk setiap atom yang mempunyai anak panah menunjukkan kepadanya, dan letakkan penghibridan tersebut di dalam kotak yang disediakan. Anggapkan bahawa setiap atom karbon mempunyai ikatan yang mencukupi dengan hidrogen untuk melengkapkan oktetnya atau untuk membolehkan cas formalnya diterima pakai.*

[a] 

[b] 

[c] 

[5 markah]

11. What is steam cracking? Briefly explain the process.

[5 marks]

11. Apakah peretakan stim? Terangkan secara ringkas prosesnya.

[5 markah]

12. Classify synthetic polymers and briefly explain each of them.

[5 marks]

12. Kelaskan polimer sintetik dan terangkan secara ringkas setiap satunya.

[5 markah]

13. What is the chemical name and structure of Aspirin? How can it be synthesized commercially?

[5 marks]

13. Apakah nama kimia dan struktur untuk Aspirin? Bagaimanakah untuk mensintesiskannya secara komersil?

[5 markah]

14. What is the difference between a synthetic surfactant and soap?

[5 marks]

14. Apakah perbezaan antara surfaktan sintetik dan sabun?

[5 markah]

15. What are the limitations in Friedel-Crafts reactions?

[5 marks]

15. Apakah kekangan-kekangan dalam tindakbalas Friedel-Crafts?

[5 markah]

...7/-

Section C : Answer any TWO questions.
Bahagian C : Jawab mana-mana DUA soalan.

16. [a] Catalytic cracking of $C_{18}H_{38}$ was carried out using a zeolite catalyst. Answer the following questions:

[i] Give the two methods which will generate $+C_{18}H_{37}$ carbocations. Give the corresponding equations associated with the production of $+C_{18}H_{37}$.

[3 marks]

[ii] Propose mechanisms for the formations of these compounds:-

(a) $H_2C = CHCH_2CH_2CH_2CH_3$

[2 marks]

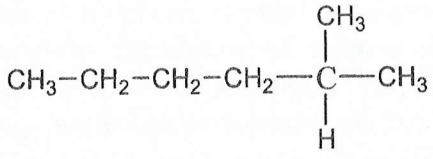
(b) $H_2C = CHCH_3$

[2 marks]

(c) C_6H_{14}

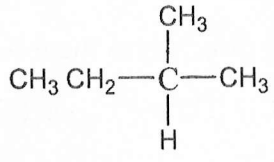
[2 marks]

(d)



[3 marks]

(e)



[3 marks]

[b] Peroxides are often added to free-radical reactions as initiators because the oxygen-oxygen bond is homolitically cleaved rather easily. Give two possible mechanisms for the hydrogen peroxide-initiated reaction of cyclopentane with chlorine.

[10 marks]

16. [a] Peretakan bermangkin bagi $C_{18}H_{38}$ telah dijalankan dengan menggunakan mangkin zeolit. Jawab soalan-soalan berikut:

[i] Berikan dua cara untuk menjana karbokation $+C_{18}H_{37}$. Berikan persamaan-persamaan yang berkaitan dengan penjanaan $+C_{18}H_{37}$.

[3 markah]

[ii] *Cadangkan mekanisma-mekanisma untuk pembentukan sebatian-sebatian berikut:-*

(a) $H_2C = CHCH_2CH_2CH_2CH_3$

[2 markah]

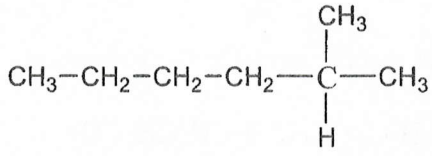
(b) $H_2C = CHCH_3$

[2 markah]

(c) C_6H_{14}

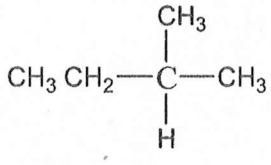
[2 markah]

(d)



[3 markah]

(e)



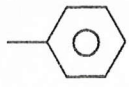
[3 markah]

[b] *Peroksida-peroksida selalunya ditambah ke dalam tindakbalas radikal bebas sebagai bahan pemula kerana ikatan oksigen-oksigen mudah dibelah atau diputuskan secara homolitik. Berikan dua kemungkinan mekanisma-mekanisma untuk tindakbalas siklopentana dan klorin yang dimulakan oleh hidrogen peroksida.*

[10 markah]

17. [a] Assign Cahn-Ingold-Prelog priorities to the following sets of substituents:-

[i] $-CH=CH_2$, $-CH(CH_3)_2$, $-C(CH_3)_3$, $-CH_2CH_3$

[ii] $-C\equiv CH$, $-CH=CH_2$, $-C(CH_3)_3$, 

[iii] $-CO_2CH_3$, $-COCH_3$, $-CH_2OCH_3$, $-CH_2CH_3$

[iv] $-C\equiv N$, $-CH_2Br$, $-CH_2CH_2Br$, $-Br$

[8 marks]

[b] Propose a mechanism for the free radical

[i] Chlorination of ethane, (show the curved arrows)

$$CH_3 - CH_3 + Cl_2 \xrightarrow{h\upsilon} CH_3CH_2Cl + HCl$$

[6 marks]

[ii] Calculate the ΔH^o (kJ/mol) for each step in this reaction.

[6 marks]

[iii] Calculate the overall value of ΔH^o (kJ/mol) for this reaction.

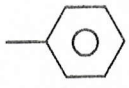
[2 marks]

[c] List 5 factors which can increase capital cost in an industrial process.

[3 marks]

17. *[a]* *Berikan keutamaan-keutamaan Cahn-Ingold-Prelog untuk set-set penukar ganti yang berikut:-*

[i] $-CH{=}CH_2$, $-CH(CH_3)_2$, $-C(CH_3)_3$, $-CH_2CH_3$

[ii] $-C{\equiv}CH$, $-CH{=}CH_2$, $-C(CH_3)_3$, 

[iii] $-CO_2CH_3$, $-COCH_3$, $-CH_2OCH_3$, $-CH_2CH_3$

[iv] $-C{\equiv}N$, $-CH_2Br$, $-CH_2CH_2Br$, $-Br$

[8 markah]

[b] *Cadangkan mekanisma untuk radikal bebas*

[i] *Pengklorinan etana (tunjukkan anak panah-anak panah melengkung)*

$$CH_3-CH_3 + Cl_2 \xrightarrow{h\upsilon} CH_3CH_2Cl + HCl$$

[6 markah]

[ii] *Kirakan ΔH^o (kJ/mol) untuk setiap langkah dalam tindakbalas ini.*

[6 markah]

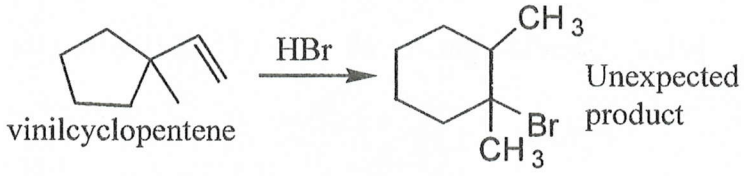
[iii] *Kirakan nilai keseluruhan ΔH^o (kJ/mol) untuk tindakbalas ini.*

[2 markah]

[c] *Senaraikan 5 faktor yang akan meningkatkan kos kapital di dalam satu proses industri.*

[3 markah]

18. [a] A routine addition of HBr across the double bond of a vinylcyclopentene gave an unexpected product. Propose a mechanism for the formation of this product.



What is the expected product?

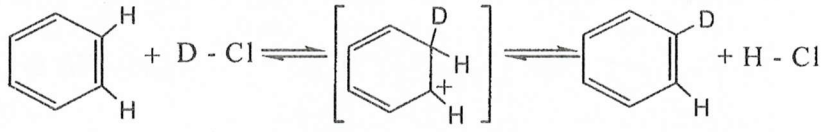
[10 marks]

[b] Give a mechanism for the reaction of the first 3 ethene molecules in the polymerization of ethene in the presence of a peroxide.

[5 marks]

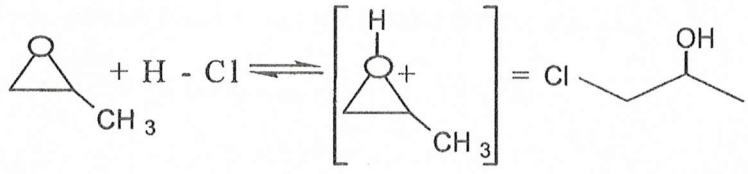
[c] Add curved arrows to the following reactions to indicate the flow of electrons in each:

[i]



[2 marks]

[ii]



[2 marks]

[d] Free radical chlorination of hexane gives very poor yields of 1-chlorohexane, while cyclohexane can be converted to chloro-cyclohexane in good yield.

[i] How do you account for this difference?

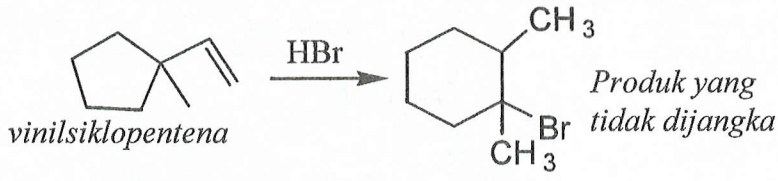
[3 marks]

[ii] What ratio of reactants (cyclohexane and chlorine) would you use for the synthesis of chlorocyclohexane? Why?

[3 marks]

...11/-

18. [a] *Penambahan HBr kepada dwi-ikatan bagi vinilsiklopentena telah menghasilkan satu produk yang tidak dijangka. Cadangkan satu mekanisma untuk pembentukan produk ini.*



vinilsiklopentena *Produk yang tidak dijangka*

Apakah produk yang dijangkakan?

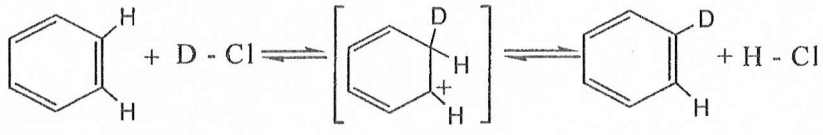
[10 markah]

[b] *Berikan mekanisma untuk tindakbalas bagi 3 molekul etena yang pertama dalam pempolimeran etena dengan kehadiran peroksida.*

[5 markah]

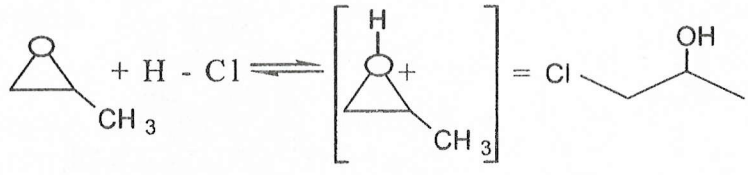
[c] *Tambahkan anak panah-anak panah melengkung untuk tindakbalas-tindakbalas berikut bagi menunjukkan pergerakan elektron:*

[i]



[2 markah]

[ii]



[2 markah]

[d] *Pengklorinan radikal bebas untuk heksana memberikan hasil yang sedikit untuk 1-kloroheksana, manakala sikloheksana boleh ditukar ke kloro-sikloheksana dengan hasil yang tinggi.*

[i] Terangkan perbezaan ini

[3 markah]

[ii] Apakah nisbah reaktan (sikloheksana dan klorin) yang akan anda gunakan untuk mensintesiskan klorosikloheksana? Kenapa?

[3 markah]

- ooo O ooo -

Lampiran

TABLE Bond-Dissociation Energies for Homolytic Cleavages

$$A{:}B \longrightarrow A\cdot + \cdot B$$

Bond	Bond-Dissociation Energy kcal/mol	kJ/mol
H—X bonds and X—X bonds		
H—H	104	435
D—D	106	444
F—F	38	159
Cl—Cl	58	242
Br—Br	46	192
I—I	36	151
H—F	136	569
H—Cl	103	431
H—Br	88	368
H—I	71	297
HO—H	119	498
HO—OH	51	213
Methyl bonds		
CH_3—H	104	435
CH_3—F	109	456
CH_3—Cl	84	351
CH_3—Br	70	293
CH_3—I	56	234
CH_3—OH	91	381
Bonds to primary carbons		
CH_3CH_2—H	98	410
CH_3CH_2—F	107	448
CH_3CH_2—Cl	81	339
CH_3CH_2—Br	68	285
CH_3CH_2—I	53	222
CH_3CH_2—OH	91	381
$CH_3CH_2CH_2$—H	98	410
$CH_3CH_2CH_2$—F	107	448
$CH_3CH_2CH_2$—Cl	81	339
$CH_3CH_2CH_2$—Br	68	285
$CH_3CH_2CH_2$—I	53	222
$CH_3CH_2CH_2$—OH	91	381
Bonds to secondary carbons		
$(CH_3)_2CH$—H	95	397
$(CH_3)_2CH$—F	106	444
$(CH_3)_2CH$—Cl	80	335
$(CH_3)_2CH$—Br	68	285
$(CH_3)_2CH$—I	53	222
$(CH_3)_2CH$—OH	91	381
Bonds to tertiary carbons		
$(CH_3)_3C$—H	91	381
$(CH_3)_3C$—F	106	444
$(CH_3)_3C$—Cl	79	331
$(CH_3)_3C$—Br	65	272
$(CH_3)_3C$—I	50	209
$(CH_3)_3C$—OH	91	381
Other C—H bonds		
$PhCH_2$—H (benzylic)	85	356
CH_2=$CHCH_2$—H (allylic)	87	364
CH_2=CH—H (vinyl)	108	452
Ph—H (aromatic)	110	460
C—C bonds		
CH_3—CH_3	88	368
CH_3CH_2—CH_3	85	356
CH_3CH_2—CH_2CH_3	82	343
$(CH_3)_2CH$—CH_3	84	351
$(CH_3)_3C$—CH_3	81	339